SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 24, No. 4, pp. 877–885, 2005
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Printed in the USA
0730-7268/05 $12.00 + .00

THE CONTRASTING ROLES OF SEDIMENTARY PLANT-DERIVED CARBON AND BLACK CARBON ON SEDIMENT-SPIKED HYDROPHOBIC ORGANIC CONTAMINANT BIOAVAILABILITY TO *DIPOREIA* SPECIES AND *LUMBRICULUS VARIEGATUS*

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(*Received* 30 *March* 2004; *Accepted* 27 *September* 2004)

Abstract—In bioavailability studies, the biota sediment accumulation factor (BSAF) is invoked to describe the thermodynamic partitioning of a hydrophobic organic contaminant (HOC) between the organism lipid and the organic carbon fraction of the sedimentary matrix and accounts for differences in bioavailability among sediments. Bioaccumulation experiments were performed with *Lumbriculus variegatus* and *Diporeia* species exposed in seven sediments dosed with 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCBP) and benzo[*a*]pyrene (B*a*P) or pyrene (PY) and 3,4,3′,4′-tetrachlorobiphenyl (TCBP). The BSAF values for the nonplanar HCBP were consistent with equilibrium partitioning theory (EQP) and averaged 2.87 for *L. variegatus* and 1.45 for *Diporeia*, while the BSAF values for the planar compounds (B*a*P, PY, TCBP) were generally lower than estimated from EQP (<1). Correcting the BSAF values of the planar compounds for enhanced sorption due to black carbon improved the BSAF values for *L. variegatus*, generally resulting in values consistent with EQP, but substantial variation remained for *Diporeia*. The BSAF values for the planar compounds showed significant positive correlations with plant-derived carbon in sediments (lignin and pigments) but were more consistent for *L. variegatus* than for *Diporeia*. These correlations imply that compounds sorbed to plant-derived carbon are more bioavailable since this material is more likely ingested providing a second exposure route.

Keywords—Black carbon   Bioavailability   Plant-derived carbon   Biota-sediment accumulation factor

INTRODUCTION

Historically, bioavailability studies have attempted to explain hydrophobic organic contaminant (HOC) bioaccumulation from sediments via factors related to HOC chemistry [1,2], organism biological response and metabolic function [3,4], and other factors related to particulate and dissolved natural organic matter composition [5–7]. Many of these studies have been based on the underlying assumption that contaminant distributions between sediments, pore waters, organisms, and their food are at equilibrium [8–10].

In an analogous manner, bioaccumulation investigations have also focused on the kinetics of HOC bioaccumulation, with the thought that HOC accumulation is a function of rate limitations ensuing from intra-aggregate HOC desorption [11–13]. Recent studies in this area suggest that HOCs are sorbed to "rapid desorbing" and "slower desorbing" pools of organic matter in sediment aggregates [13–16]. This approach has indicated that the most rapidly desorbing pool of an HOC from a particle aggregate may be the most relevant with respect to HOC bioaccumulation [12–14,17,18]. In that context, Shor et al. [19] have presented a systematic view of polycyclic aromatic hydrocarbon (PAH) desorption kinetics from sedimentary particles as a function of sediment grain size, composition, and PAH hydrophobicity in which they state that the magnitude of the readily desorbable fraction of a PAH can be predicted using a simple 24-h assay. Thus, if rapidly desorbing HOC concentrations are correlated to contaminant bioaccumulation and bioavailability, then evaluating factors that most directly control rapid desorption from a sediment aggregate should lead to an understanding of the characteristics that control the bioavailability and subsequently the bioaccumulation of sediment-associated contaminants.

A large number of geosorbents may contribute to both the sorption and the desorption of organic contaminants to sedimentary particles [20,21]. Recent studies have suggested particularly strong sorption and, by inference, limited desorption of contaminants from condensed refractory organic matter, black carbon (BC), in both field-collected sediments and laboratory studies [22–24]. Thus, the presence of BC in sedimentary systems may substantially limit bioavailability of sediment-associated organic contaminants. Two recent works, one involving laboratory-sorbed phenanthrene to sediments amended with BC [25; http://www.wes.amry.mil/el/dots/eedptn.html] and one examining the bioavailability of environmentally resident pyrogenic and petrogenic PAH with the amendment of differing types of BC [26], suggest that BC is a strong sorbent for pyrogenic PAH and substantially reduces their bioavailability. However, from the same study, BC was not a super sorbent for petrogenic PAH and did not reduce their bioavailability beyond that expected although EQP [26].

Another type of geosorbent in natural systems is plant-derived organic matter. Although nonpolar organic contaminants often demonstrate low partition coefficients to plant-

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Table 1. Sediment sampling stations and variables pertaining to sediment geochemistry at each sampling station. See text for explanations from Kukkonen et al. [16]; latitude and longitude are given as degrees.minutes.seconds[a]

Sediment	North latitude	West longitude	$f_{TOC} \times 10^2$	$f_{BC} \times 10^4$	$f_{Lignin} \times 10^5$	$f_{Chl\ A} \times 10^6$	$f_{Lipid} \times 10^6$	% OC >420 μm	% OC <63 μm
Lake Michigan	43.01.48	86.22.12	0.41 ± 0.01	3.0 ± 1.0	6.7 ± 0.60	0.19 ± 0.04	8.6 ± 3.5	1.7	79.5
Lake Huron Station 9	43.38.00	82.13.00	3.71 ± 0.15	27 ± 1.0	9.8 ± 2.8	0.33 ± 0.04	17.9 ± 5.2	0.8	82.5
Lake Huron Station 54	45.31.00	83.25.00	3.18 ± 0.05	32 ± 1.0	5.9 ± 0.2	0.36 ± 0.05	20.4 ± 4.7	1.3	94.5
West Bearskin	48.03.56	90.25.38	1.25 ± 0.26	5.0 ± 1.0	40 ± 7.0	0.73 ± 0.09	10.0 ± 2.3	2.2	90
Terwilliger's Pond	41.39.24	82.49.39	4.11 ± 0.37	25 ± 2.0	230 ± 61	6.8 ± 0.04	53.5 ± 0.14	7.55	59.9
Lake Erie	41.39.48	82.49.46	1.82 ± 0.05	16 ± 1.0	8.8 ± 5.0	3.11 ± 0.34	40.5 ± 10.4	0.9	94.3
Pond 5	39.00.00	92.15.00	3.00 ± 0.27	16 ± 1.0	140 ± 90	10.8 ± 0.90	49.9 ± 7.5	8.7	65.1

[a] f_{TOC} = fraction total organic carbon (OC); f_{BC} = fraction black carbon; f_{Lignin} = fraction of the total lignin in sediment; $f_{Chl\ A}$ = the fraction of chlorophyll-*a*; f_{Lipid} = the fraction of lipid like material in the sediment; % OC >420 μm = the percent of total organic carbon in the particle size fraction >420 μm; and % OC <63 μm is the percent of total organic carbon found in the <63-μm particle size fraction of the sediment.

derived materials such as cellulose (see review [21]), other plant-derived components are effective sorbants [27–29]. Such plant-derived materials have demonstrated a positive relationship with the fraction of compound that is rapidly desorbed [16]. Plant-derived organic material also constitutes a major food source for most heterotrophic benthic invertebrates. Selective feeding on contaminants sorbed to plant-derived organic matter of high nutritious quality can increase their bioaccumulation and generate body burdens above those predicted by simple partitioning in deposit-feeding organisms [30]. Thus, plant-derived material, both through its role as a sorbent for HOC and as a potential vector of HOC through dietary exposure, may be a better predictor of bioavailability than the amount of BC in sediments.

Our objective was to address HOC bioavailability to two benthic invertebrates, *Lumbriculus variegatus* and *Diporeia* species, from sediments differing in their composition collected from seven geographical locations. The main emphasis was to evaluate the relationship between benthic bioaccumulation and two specific compositional variables: sedimentary plant-derived organic matter and sedimentary BC. In this study, we use chlorophyll and lignin to represent plant-derived organic matter.

MATERIALS AND METHODS

The collection, characterization, spiking, organism exposures, and toxicokinetics have been previously described in detail [16,18]. Thus, the experimental details are provided here in only a brief format, and the details may be obtained from the previously mentioned references.

Sediment collection and characterization

Sediments were collected from seven locations: Lake Erie (OH, USA), Lake Huron (MI, USA), Lake Michigan (MI, USA), West Bearskin Lake (MN, USA), Terwilliger's Pond (OH, USA), and a pond in Columbia (MO, USA) named Pond 5 (Table 1). Sediment characteristics, including the amount of organic carbon (OC), BC, plant pigments including chlorophyll-*a*, lipid-like compounds, lignin, and sediment particle size, were measured. In brief, sediment BC content was measured using the thermal oxidation method described by Gustafsson et al. [31] and is analytically defined as the residual carbon after thermal oxidation of sediment at 375°C for 24 h to remove labile carbon followed by acidification with 2 N HCl [31]. Sedimentary OC was determined after removing carbonates with HCl. Both OC and BC were quantified by combusting samples in an EA 1110 CHN analyzer (CE Instruments, Thermoquest Italia, Milan, Italy). Sedimentary lignin was measured using the cupric oxide method of Hedges and Ertel [32]. The mass fraction of the sum of six lignin-phenol monomers (acetovanillone, vanillic acid, vanillin, acetosyringone, syringic acid, syrinaldehyde) per dry weight of sediment was quantified. Plant pigments were extracted using ethanol, and chlorophyll-*a* was quantified by fluorescence [33]. The content of lipid-like materials was determined by extracting a freeze-dried aliquot of sediment with chloroform methanol (2:1) and analyzing the extract spectrophotometrically using the method of Van Handel [34].

Sediment spiking

The sediments were spiked in equimolar concentrations at 360 nmol/kg with four radiolabeled HOCs in two treatment groups including one PAH and one polychlorinated biphenyl congener in each treatment. The four radiolabeled HOCs were ^{3}H-pyrene (PY, specific activity 25.2 Ci/mmole), ^{14}C-3,3′,4,4′-tetrachlorobiphenyl (TCBP, specific activity 12.5 mCi/mmole), ^{3}H-benzo[*a*]pyrene (B*a*P, specific activity 50.0 Ci/mmole), and ^{14}C-2,2′,4,4′,5,5′-hexachlorobiphenyl ([HCBP], specific activity 12.6 mCi/mmole). Nonlabeled PY (purity >99%) and B*a*P (purity >98%) obtained from Aldrich (Milwaukee, WI, USA) were added with the radiolabeled compounds to limit the amount of radioactivity required. The sediments were spiked using the rolling jar method with slight modification, and subsamples were taken for direct liquid scintillation counting after sonication. The measured concentrations based on the specific activities of the compound, including accounting for the isotopic dilution of the tritiated compounds, averaged 390 ± 30 nmol/kg for B*a*P, 370 ± 30 nmol/kg for HCBP, 340 ± 20 nmol/kg for PY, and 350 ± 20 nmol/kg for TCBP. The HOCs were allowed to sorb to sediments for 60 to 110 d, after which the sediments were placed in microcosms. The particle size distribution of the sediments was determined by wet sieving through sieves with 420-, 105-, 63-, 37-, and 20-μm mesh. The dry weight, concentration of the model compounds, and OC for each particle size fraction were determined in the same manner as for the whole sediment. The log octanol–water partition coefficient (log K_{OW}) for PY, TCBP, B*a*P, and HCBP were, respectively, 5.13, 6.50, 6.13, and 7.15 [35].

Bioaccumulation assays

Lumbriculus variegatus were laboratory cultured, while *Diporeia* species were collected from Lake Michigan at a 60-m-deep station west of Muskegon, Michigan, USA (43°10.92′N, 86°26.96′W) [18]. For the *Diporeia* assay, the sediments (45 g) and 300 ml Huron River Water (Dexter, MI, USA) were distributed into 400-ml beakers, with 18 beakers per sediment type. Eight *Diporeia* were added to each beaker after settling overnight. The exposures were at 4°C in the dark, and three replicate beakers were sampled after approximately 2, 4, 8, 14, 21, and 28 d. Two *Diporeia* per beaker were taken for lipid content on days 2, 14, and 28 and analyzed by a spectrophotometric method [34]. Two replicates of three to four *Diporeia* from each beaker were prepared for determination of contaminant concentration. The *Diporeia* were blotted dry, weighed, and dispersed into 1 ml of tissue solubilizer (Soluene 350, Packard, Meriden, CT, USA) for 24 h before the addition of 12 ml scintillation cocktail. A sediment sample was taken for measurement of compound concentrations as described previously. Another sediment subsample was dried at 90°C to determine the wet-weight:dry-weight ratio.

For *L. variegatus*, 45 g of wet sediment were transferred into 250-ml beakers. Ten test organisms were added to each beaker after settling overnight. The exposure was at 20°C and used the water renewal system described by Zumwalt et al. [36] with half the volume of overlying water exchanged daily. Three replicate beakers were sampled after approximately 1, 2, 4, 7, 11, and 14 d. These samples were treated as described previously for *Diporeia*.

Bioaccumulation data

The accumulation data were fit to a first-order accumulation model to estimate the uptake clearance, k_s (g dry sediment/g organism/h) and the elimination rate constant, k_e (per hour):

$$C_a = \frac{k_s}{k_e}\frac{C_s}{}(1 - e^{-k_e t}) \quad (1)$$

where C_a = concentration of the compound in the organism (ng/g wet-wt organism), C_s = concentration of the compound in the sediment (ng/g dry wt), k_s = the uptake clearance of the compound from sediment (g dry sediment/g wet organism/h), k_e = the elimination rate constant of the compound (per hour) in sediment, and t = time (h). The model assumes that the concentration in the sediment remains constant and that no biotransformation of the compound occurs. The data were fit by nonlinear curve fitting using Scientist® (MicroMath Scientific Software, St. Louis, MO, USA).

The BSAF was determined by normalizing the steady-state BAF determined as the ratio of k_s/k_e by the sediment OC content and the organism lipid content [18]. The BSAF values were corrected for the potential binding to BC in a manner similar to Equation 2 in Thorsen et al. [26]:

$$\mathrm{BSAF_{Corr}} = \mathrm{BSAF}\cdot\left(\frac{f_{\mathrm{POC}} + f_{\mathrm{BC}}\dfrac{K_{\mathrm{BC}}}{K_{\mathrm{OC}}}}{f_{\mathrm{TOC}}}\right) \quad (2)$$

where f_{POC} is the fraction of plant-derived OC calculated as the fraction of total organic carbon (f_{TOC}) minus the fraction of BC (f_{BC}), K_{BC} is the partition coefficient for BC, and K_{OC} is the conventional binding to non-BC sediment OC. Because K_{OC} was not measured directly, K_{OW} was substituted because K_{OW} is essentially equal to K_{OC} [9]. Estimates for log K_{BC} were derived for B*a*P (7.7) and PY (6.8) from a regression using the data in Bucheli and Gustafsson [37] and for TCBP (7.5) and HCBP (8.1) using the regression in Bucheli and Gustafsson [38]. The polychlorinated biphenyl regression was for non-*ortho* congeners. Because no good data existed for ortho congeners, the regression for non-*ortho* congeners was applied for both types of polychlorinated biphenyl compounds.

Linear regressions were performed using the reduced major axis approach, sometimes called the geometric mean functional regression, to account for the fact that both the *x*- and the *y*-axis variables have measurement error [39]. Regressions were considered significant at $p < 0.05$.

RESULTS

The sediments in this work were well characterized for a range of geochemical characteristics (Table 1). The lipid content of the organisms were 1.5 ± 0.19% (PY/TCBP) and 1.2 ± 0.13% (B*a*P/HCBP) for *L. variegatus* and 6.2 ± 1.4% (Py/TCBP) and 5.5 ± 0.7% (B*a*P/HCBP) for *Diporeia* on a wet-weight basis [18]. The sediment characteristics were correlated to bioaccumulation factors to investigate differences in bioavailability between the sediments for the four spiked contaminants. As noted previously, the two variables specifically examined in this study were BC, which was expected to reduce bioavailability, and plant-derived organic materials, that is, lignin and chlorophyll-*a*, which were thought to serve as a food source and enhance exposure.

Black carbon

The BSAF value should be unity if the chemical capacity of the OC is equivalent to the chemical capacity of the lipid in the organism. A calculated theoretical value of 1.7 has been suggested for the BSAF [40,41], suggesting a larger capacity for organism lipid than for sediment OC. For *L. variegatus*, the BSAF calculated with the total sediment OC (Table 2) averaged 2.87 ± 0.6 for HCBP. However, the average values were <1 for all the planar compounds with a few values of 1 or greater particularly for sediments from Terwilliger's Pond and Pond 5 sediments. Thus, the planar compounds, which should be more susceptible to enhanced sorption by BC, might yield a value of 1 or greater if corrected for the additional sorption capacity of BC. Only the BSAF values for the planar compounds were corrected for BC, as the HCBP was not apparently affected since the average value was greater than 1. Once corrected, all the $\mathrm{BSAF_{Corr}}$ values were similar to or greater than 1 except for the West Bearskin Lake sediments for *L. variegatus* (Table 2). The West Bearskin Lake sediment has very low BC concentrations but still exhibited strong limitations to bioavailability. Thus, the correction for BC appears to create BSAF estimates that are more consistent with EQP. However, the BSAF values that were at or above 1 before correction are now substantially larger and in the case of PY are 4.7 or greater, suggesting that these values have been overcorrected.

For *Diporeia*, the average BSAF was lower than for *L. variegatus* for HCBP, but the average was >1 at 1.45 ± 0.89. Thus, for the most part, HCBP partitioning to these sediments appears to occur in a manner following thermodynamics. For the planar compounds with *Diporeia*, the PY and TCBP both follow the same pattern as *L. variegatus* with values for BSAF generally <1 but those from Terwilliger's Pond and Pond 5 greater than 1. For B*a*P, there were no BSAF values greater than 1 (Table 2). Correction for BC yielded $\mathrm{BSAF_{Corr}}$ values that averaged above 1 for TCBP and PY with only the West Bearskin Lake sediment substantially below 1 for PY. However, for TCBP, about half the $\mathrm{BSAF_{Corr}}$ values remained below 1, and more than half the values were below 1 for B*a*P. The West Bearskin Lake sediment remained below 1 for all the

Table 2. Biota-sediment accumulation factors (BSAF) for the selected polychlorinated biphenyl and polycyclic aromatic hydrocarbon congeners from Kukkonen et al. [18][a]

Sediment	Lv–BSAF HCBP	Lv–BSAF *Ba*P	Lv–BSAF TCBP	Lv–BSAF PY	Lv–$BSAF_{Corr}$ *Ba*P	Lv–$BSAF_{Corr}$ TCBP	Lv–$BSAF_{Corr}$ PY
Lake Michigan	2.25	0.37	0.52	0.52	1.51	0.84	2.07
Lake Huron 9	3.61	0.23	0.79	0.29	0.94	1.28	1.15
Lake Huron 54	3.3	0.50	1.07	0.74	2.62	2.00	3.77
West Bearskin Lake	2.94	0.13	0.37	0.29	0.35	0.49	0.76
Terwilliger's Pond	3.17	1.00	2.14	1.34	3.56	3.26	4.66
Lake Erie	1.95	0.50	0.86	0.66	2.35	1.51	3.02
Pond 5	2.87	1.34	2.24	2.03	4.35	3.27	6.44
	Dip–BSAF HCBP	Dip–BSAF *Ba*P	Dip–BSAF TCBP	Dip–BSAF PY	Dip–$BSAF_{Corr}$ *Ba*P	Dip–$BSAF_{Corr}$ TCBP	Dip–$BSAF_{Corr}$ PY
Lake Michigan	0.61	0.05	0.16	0.22	0.20	0.26	0.88
Lake Huron 9	1.42	0.03	0.47	0.27	0.12	0.77	1.07
Lake Huron 54	1.08	0.04	0.26	0.37	0.21	0.49	1.88
West Bearskin Lake	1.06	0.01	0.14	0.16	0.03	0.19	0.42
Terwilliger's Pond	2.74	0.22	2.19	1.57	0.78	3.34	5.46
Lake Erie	0.62	0.06	0.39	0.41	0.28	0.69	1.87
Pond 5	2.64	0.40	2.45	1.62	1.30	3.58	5.14

[a] BaP = benzo[*a*]pyrene; PY = pyrene; HCBP = hexachlorobiphenyl; TCBP = tetrachlorobiphenyl; Lv = *L. variegatus*; Dip = *Diporeia* spp.; BASF = biota-sediment accumulation factor with organism concentrations normalized to lipid content and sediment concentrations normalized to total organic carbon content; and $BSAF_{Corr}$ = BSAF corrected for BC partitioning.

planar compounds even after BC correction. As with *L. variegatus*, the corrected BSAF values, particularly for PY, are large (greater than 5), which suggested overcorrection for this compound. Overall, for both organisms, correction for the amount of BC increased the BSAF values but did not consistently provide values near an expected theoretical thermodynamic partitioning value of 1 to 2.

Chlorophyll-a

For the three planar compounds, B*a*P, PY, and TCBP, three sediment geochemical characteristics provided positive correlations with BSAF for both species: plant pigments as represented by chlorophyll-*a* or total pigments, the lipid-like material in sediments, and total lignins. These sediment characteristics covary so that using one of the variables to describe the variation in BSAF serves as an example for all. For HCBP, only the *Diporeia* BSAF exhibited significant correlations with pigment and lipid-like material content in sediments, while none of these features produced significant correlations for *L. variegatus* (Table 3). Within the three planar compounds, chlorophyll-*a* was generally more predictive of bioavailability differences among the sediments as exhibited by the larger correlation coefficients compared to those for lipid-like material and lignins (Table 3). For the planar compounds, chlorophyll-*a* accounted for about 70% of the variation in the BSAF across all sediments for *L. variegatus* (Fig. 1). For *Diporeia*, chlorophyll-*a* accounted for only about half the variation in BSAF for all the planar compounds combined across all sediments (Fig. 2). For *Diporeia*, the r^2 values for regressions across all sediments for each of the planar compounds independently was much better (r^2 = 0.89–0.95) than for all the compounds together, although the slopes of the regression lines ranged from 0.03 for BaP to 0.23 for TCBP. This range of slopes results in the lower r^2 value compared to *L. variegatus* when the data from all compounds were regressed together for each organism. Thus, while chlorophyll-*a* explained the variation

Table 3. Pearson correlation coefficients between biota-sediment accumulation factor (BSAF) and sediment characteristics for each compound and organism across the seven sediments (n = 7)[a]

Organism/compound	Chlorophyll-*a*	Lipid	Lignin	% OC >420	% OC <63
LV–B*a*P	0.95	0.87	0.78	0.91	−0.76
LV–HCBP	NS[b]	NS	NS	NS	NS
LV–PY	0.95	0.82	0.76	0.92	−0.73[c]
LV–TCBP	0.91	0.89	0.87	0.91	−0.80
DIP–B*a*P	0.98	0.79	0.77	0.94	−0.79
DIP–HCBP	0.83	0.74[c]	0.92	0.92	−0.87
DIP–PY	0.95	0.89	0.92	0.96	−0.86
DIP–TCBP	0.95	0.86	0.91	0.97	−0.89

[a] LV = *Lumbriculus variegatus*; DIP = *Diporeia* spp.; B*a*P = benzo[*a*]pyrene; HCBP = hexachlorobiphenyl; PY = pyrene; TCBP = tetrachlorobiphenyl; % OC >420 = percent of the total organic carbon on particles greater than 420 μm diameter; % OC <63 = percent of total organic carbon on particles less than 63 μm diameter.
[b] NS = not significant.
[c] Correlation coefficient is significant at p = 0.06; all other correlation coefficients significant at $p <$ 0.05.

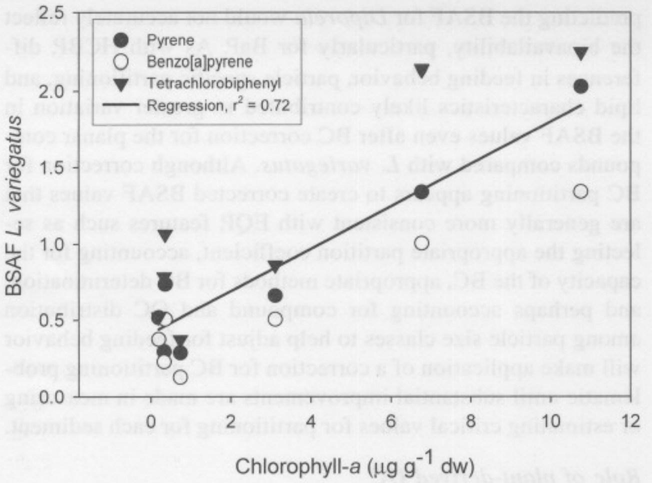

Fig. 1. Regression of the biota-sediment accumulation factor (BSAF) for *Lumbriculus variegatus* as a function of the amount of chlorophyll-*a* (CHLA; µg/g dry-wt sediment) in the sample for the three planar compounds. BSAF = 0.17(0.02)·CHLA + 0.31(0.014), $n = 21$, $r^2 = 0.71$, $p < 0.05$. Numbers in parentheses represent standard error from regression. dw = dry weight.

across sediments relatively well, a between-compound variability existed that was not well accounted for in *Diporeia*. For the two PAHs, the slope for PY was greater than that for B*a*P, suggesting that the PY was more available per amount of chlorophyll-*a*, likely reflecting a weaker association between pyrene and chlorophyll-*a*. No obvious factor explained the variation between B*a*P and TCBP, which have similar log K_{OW} values.

Particle size

Another feature of the sediment that was correlated with the BSAF was the amount of contaminant and OC found on various particle size fractions. Contaminants and OC were found to be selectively associated with specific size classes, but OC and contaminants did not necessarily distribute in the same proportion to the same-size particles [16]. Differences

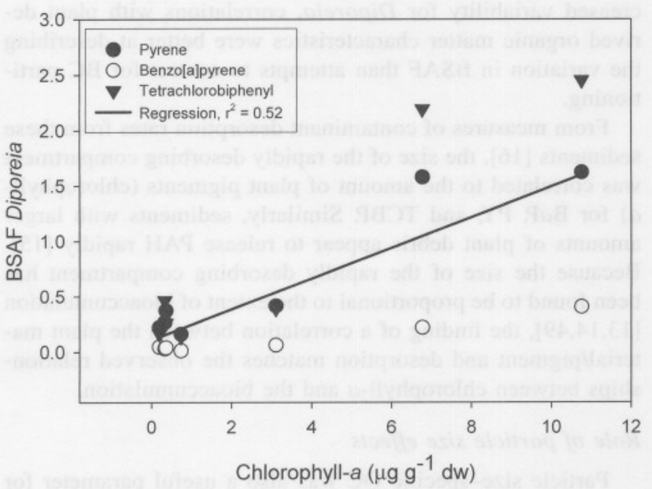

Fig. 2. Regression of the biota-sediment accumulation factor (BSAF) for *Diporeia* species as a function of the amount of chlorophyll-*a* (CHLA; µg/g dry-wt sediment) in the sample for the three planar compounds. BSAF = 0.19(0.03)·CHLA − 0.06(0.03), $n = 21$, $r^2 = 0.52$, $p < 0.05$. Numbers in parentheses represent standard error from regression. dw = dry weight.

in the size-selective distribution among particles for the different sediments may contribute to the overall variation in bioavailability of the compounds across sediments. A distinctive feature in this study was the role of the OC content for >420-µm-size particles. This feature was positively correlated with the BSAF for the planar compounds for both species and for HCBP in *Diporeia* (Table 3). Since particles of this size are not ingested by either organism because they are too large, the influence of this size class of particles on the bioavailability likely relates to the desorption of the compound to the interstitial water. Although this potential mechanism is hypothetical, a simple redistribution between course and fine particles did not seem to explain differences in bioavailability. For instance, while the distribution of the compounds was greater on the small particle size fraction (particles <63 µm diam [16]), the BSAF was often negatively correlated with the fraction of OC in fine particles (Table 3). This suggests that the greater the OC in the fine material, which is in the size range that the organisms ingest, the lower the bioavailability. However, greater OC content within a particle class did not always lead to lower bioavailability as represented by the positive Pearson correlation coefficients for the >420-µm-size particles.

DISCUSSION

The traditional conceptual understanding of the bioavailability of contaminants from sediments has been described with the calculation or measurement of the bioaccumulation factor (BAF) as a steady-state ratio of the concentration in organisms divided by the concentration in the sediment, or as the ratio of the uptake and elimination rate coefficients [42]. For nonpolar organic contaminants using EQP to predict exposure [9], it was recognized that differences in lipid content among species and differences in the amount of OC would alter the BAF reflecting the chemical capacity in each compartment. Thus, normalizing the BAF to organism lipid and sediment OC creating a BSAF was developed as a means to remove the variability between sediments and organisms.

Role of black carbon

Recent efforts have shown that the composition of OC can affect both the distribution of the contaminant between sediment particles (e.g., [23,38]) and the bioavailability of organic contaminants (e.g., [6,43]). Thus, it is clear that the bioavailability of nonpolar organic contaminants depends on both organism and sediment geochemical characteristics. Without accounting for BC partitioning, the HCBP BSAF values were generally consistent with EQP in that the BSAF was essentially constant across the range of sediments and the values were generally in the range of 1 to 2 for both species (Table 2). The average *L. variegatus* BSAF for HCBP of 2.87 ± 0.6 was only somewhat larger than the expected value of 1.7 from theoretical calculations [40,41], while that for *Diporeia* was somewhat smaller, 1.45 ± 0.89. The higher average value for *L. variegatus* compared to the theoretical calculation suggests the potential impact of feeding on contaminated particles as an additional transport mechanism enhancing bioaccumulation above that expected from EQP [44]. For both organisms, EQP represents an adequate model for describing the bioaccumulation potential for HCBP. The differences in the values between the two species may reflect differences in feeding behavior on fine particles and perhaps differences in physiology. Though both species ingest fine particles, generally less than

63 μm, oligochaetes are not specific feeders and take in essentially all particles small enough to be ingested. These organisms demonstrate less than a factor of two differences in OC between feces and sediment [45]. *Diporeia*, however, are considered very selective feeders [46]. Thus, if compounds are preferentially associated with specific particles [16,43], then *Diporeia* may be selecting particles that are less contaminated than the average particle ingested by *L. variegatus*. In addition to the differences in feeding behavior, the two species have substantially different lipid contents with *Diporeia* containing four- to fivefold larger lipid concentrations. The higher lipid content reflects a difference in the ratio of storage lipid to structural lipid, which might account for differences in compound capacities between the two species when concentrations are normalized to lipid.

Using the average value for HCBP BSAF in each species to respectively represent the value expected from EQP theory, the BSAF values for the planar compounds (B*a*P, PY, TCBP) were generally less than expected from EQP. However, the BSAF values for sediments from Twilliger's Pond and Pond 5 were similar to those for the average HCBP values in the respective organisms for PY and TCBP and for B*a*P in *L. variegatus*. Using the estimated partition coefficients for BC and the amount of BC in the sediments, corrected BSAF values were calculated that were generally more consistent with EQP, particularly for *L. variegatus* (Table 2). However, inconsistencies with EQP remained for both species. The BSAF values for West Bearskin Lake sediment were consistently below 1 even after BC correction for both species. Thus, either the partition coefficient selected for the BC was incorrect for this sediment or another partitioning phase that is not BC has a substantial impact on bioavailability. It has been shown that the partition coefficient to different types of BC can vary substantially, up to three orders of magnitude [47]. While it is not possible to rule out partitioning to a phase other than BC, the type of BC in each of the sediments is not known; thus, it remains unknown whether the K_{BC} selected for BSAF correction represents the specific variety of BC for each sediment. A similar argument can be made for the apparent overcorrection resulting in very large BSAF values for the Twilliger's Pond and Pond 5 sediments, particularly for PY with both species. By selecting a partition coefficient that is too large for the type of BC, an overcorrection would occur. Similarly, selecting a partition coefficient that is too small would result in an undercorrection. In the case of the apparent overcorrection, a second factor, the capacity limit of the BC, may have contributed to the larger values. Like natural organic matter, BC also has been found to possess a finite sorption capacity for HOCs [24]. Thus, those corrected BSAF values that are greater than expected from EQP could result from either the selected partition coefficient for correction or appropriate accounting for the capacity of the BC. An additional difficulty in making the BC correction is based on accurate quantification of BC in sediment. Our study followed the original thermal oxidation procedure for the isolation of BC [31] and its measurement, and some suggestion exists in the literature that this method possesses inherent artifacts [48].

While correcting for the expected partitioning by BC produced BSAF values in *L. variegatus* that were more consistent with EQP, the results for *Diporeia* were substantially less consistent (Table 2). In the case of BaP and TCBP, half or less of the corrected BSAF values were near or above a value of 1 (Table 2). Thus, applying a correction for partitioning and predicting the BSAF for *Diporeia* would not accurately reflect the bioavailability, particularly for BaP. As with HCBP, differences in feeding behavior, particle specific partitioning, and lipid characteristics likely contributed to greater variation in the BSAF values even after BC correction for the planar compounds compared with *L. variegatus*. Although correction for BC partitioning appears to create corrected BSAF values that are generally more consistent with EQP, features such as selecting the appropriate partition coefficient, accounting for the capacity of the BC, appropriate methods for BC determination, and perhaps accounting for compound and OC distribution among particle size classes to help adjust for feeding behavior will make application of a correction for BC partitioning problematic until substantial improvements are made in measuring or estimating critical values for partitioning for each sediment.

Role of plant-derived OC

For both species with respect to the planar compounds, a significant correlation was observed between BSAF and several measures that describe characteristics of plant-derived organic matter (e.g., chlorophyll-*a*, total plant pigments, and lignin). For *L. variegatus*, the regression between chlorophyll-*a* and BSAF accounts for 70% of the variation in the data and would result in a standard error of the BSAF estimate of 0.34 (~40% of mean value). The three compounds have similar slopes (0.10 ± 0.02 for BaP, 0.17 ± 0.03 for TCBP, and 0.15 ± 0.02 for PY). Still, about 30% of the variation not explained by this regression seems to be manifested in the differences in the intercepts with B*a*P having the lowest intercept and TCBP the largest. For *Diporeia*, a significant regression exists for the three planar compounds with chlorophyll-*a*, but only 50% of the variance is accounted for by the regression, resulting in a standard error of the BSAF estimate of 0.51, or about 100% of the mean BSAF. For *Diporeia*, the slopes of the regressions for the individual compounds were very different, while the intercept was the same. It is clear in this case that some additional as-yet-unidentified variable(s) account for differences in the bioavailability among the compounds. The additional variability in the prediction of *Diporeia* accumulation may result from its feeding specificity and the unequal partitioning among the particles. However, even with the increased variability for *Diporeia*, correlations with plant derived organic matter characteristics were better at describing the variation in BSAF than attempts to correct for BC partitioning.

From measures of contaminant desorption rates from these sediments [16], the size of the rapidly desorbing compartment was correlated to the amount of plant pigments (chlorophyll-*a*) for B*a*P, PY, and TCBP. Similarly, sediments with larger amounts of plant debris appear to release PAH rapidly [15]. Because the size of the rapidly desorbing compartment has been found to be proportional to the extent of bioaccumulation [13,14,49], the finding of a correlation between the plant material/pigment and desorption matches the observed relationships between chlorophyll-*a* and the bioaccumulation.

Role of particle size effects

Particle size–specific OC was also a useful parameter for evaluating the bioavailability of the planar compounds and HCBP to *Diporeia* species (Table 3). The OC on the fine particles (<63 μm) appeared to have stronger binding such that increases with the amount of carbon in this fraction reduced the bioavailability of the compounds. However, this was not a very strong relationship based on the relatively low correlation coefficients (Table 3). The reduced bioavailability suggests stronger binding capacity of the OC but may have also partly been due to larger surface area. Unfortunately, the characteristics of the OC in the particle size fractions were not determined for comparison to the characteristics from whole sediment. The opposite trend was observed for the amount of OC on the larger-size particles (>420 μm) leading to increased bioaccumulation. In this case, the correlation is likely related to the desorption of the compound off the particles since the particles are too large to be ingested by these organisms. While these correlations were significant, the data tended to cluster with two of the sediments having high BSAF values and the rest having low BSAF values, creating strong correlations but not an even distribution of the data along the *x*-axis. Further, as with the chlorophyll, the data had to be evaluated on a compound-by-compound basis, and the correlation observed across compounds was not as good as was observed using chlorophyll-*a*.

Compound characteristics

The mix of compounds in this study was primarily planar with a single nonplanar compound, HCBP. A difference clearly existed in the behavior of HCBP, which exhibited bioavailability more consistent with EQP than the planar compounds, and the planar compounds that required BC corrections or correlation with other sediment characteristics (e.g., chlorophyll-*a*) to explain the variation in the BSAF among sediments. Similarly, in previous studies, nonplanar polychlorinated biphenyl congeners, specifically HCBP and 2,4,2′,4′-tetrachlorobiphenyl, were found to respond more consistently with EQP theory than B*a*P and PY, which required correlation with organic matter quality, specifically the C/N ratio, to account for bioavailability differences among sediments [6]. On the assumption that larger C/N ratios indicate a greater amount of plant-derived carbon, both studies would support the positive impact of plant-derived carbon on the bioavailability of planar compounds. A larger C/N ratio would be consistent with a greater abundance of plant-derived carbon, as material such as cellulose does not contain nitrogen in the structure. Overall, the nonplanar compounds appeared to adhere to EQP, while the planar compounds required accounting for different characteristics of the OC to address bioavailability differences among sediments.

Organism feeding behavior

The impact of feeding behavior of the two organisms, despite both likely feeding on fine particles generally less than 63 μm, was most dramatic for HCBP, where the BSAF was correlated with several sediment characteristics for *Diporeia*. Further differences in feeding behavior may also account for some of the differences in the amount of variance accounted for by sediment characteristics such as chlorophyll-*a* with the overall regressions for the planar compounds (Figs. 1 and 2). As a selective feeder, *Diporeia* may not have been exposed to the same extent as *L. variegatus* based on the particle-selective distribution of contaminants [16] and differences in selective feeding behavior. The feeding rate and digestibility of the ingested particles combined with the differential distribution of contaminants among particles may contribute significantly to the observed correlations with the measured sediment characteristics. Certainly, it is expected that particles high in chlorophyll should represent more nutritious and digestible organic matter, perhaps enhancing the contaminant absorption efficiency with gut passage and contributing to the correlation found with chlorophyll-*a*. In contrast, the increased fraction of organic matter in fine particles could reduce the need to ingest as much sediment to meet nutritional requirements and, therefore, contribute to the reduced uptake with increasing OC content in fine sediments. Thus, differences in the feeding behavior, size of the particles containing the OC and contaminants, and the character of the OC are important for determining the overall bioavailability.

CONCLUSION

Overall, the bioavailability of the nonplanar compound, HCBP, depended most on the total amount of OC in the sediment, while the planar compounds depended more on the OC quality with a positive correlation between chlorophyll-*a* and BSAF. Correcting BSAF for HOC-BC partitioning provided values that fit EQP theory for *L. variegatus* but were less successful for *Diporeia*. However, corrections for BC partitioning should be applied cautiously because of limits to define the specific partitioning coefficient for BC for each sediment, the potential capacity limitations of BC, and the methodological problems in measuring BC specifically to define the type of BC in sediments. Unexplained variability between compounds remains, especially for the more selective-feeding *Diporeia*, indicating that some additional feature(s) of sediment contaminant interaction are not well described by the characteristics explored in this work (e.g., chlorophyll-*a* and particle size). The concept of differing compartments, rapidly and slowly desorbing, controlling the desorption and thus ultimately the bioavailability, combined with differential contaminant distribution among particles, yields a view of contaminant distribution within the sediments that is heterogeneous, and contaminants sorbed to plant-derived organic matter are apparently more responsible for the bioavailability of sediment-associated contaminants, particularly for the planar compounds.

Acknowledgement—This work was supported in part through the National Research Council and the Academy of Finland, Grant 48626. We wish to thank D. Mount (U.S. Environmental Protection Agency, Duluth, MN), C. Ingersoll (U.S. Geological Survey, Columbia, MO), T. Nalepa (Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration, Ann Arbor, MI, USA), and J. Hageman (Stone Laboratory, Put-In-Bay, OH, USA) for assistance in collecting sediments. Great Lakes Environmental Research Laboratory Contribution 1326.

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